



# Atmospheric Reactivity of Volatile Organic Compounds (VOCs)

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## Subcontract Number

ZF-2-12252-07

## Performance Period

8/93–12/95

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## Objectives

- Provide environmental chamber data to reduce uncertainties in estimates of atmospheric ozone impacts of current and alternative fuel vehicle emissions.
- Fill gaps in the environmental chamber database for evaluating gas-phase chemical mechanisms for ambient air quality models
- Evaluate effects of environmental conditions on ozone impacts of VOCs.

## Approach

- Use environmental chamber experiments to measure changes in ozone formation and VOC consumption rates caused by adding representative VOCs to simulated photochemical smog systems. Vary  $\text{NO}_x$  to total VOC ratios and the composition of the other VOC pollutants (base reformulated oxygenated gasoline [ROG] surrogate).
- Conduct experiments with relatively high  $\text{NO}_x$ /base ROG ratios to test the Maximum Incremental Reactivity (MIR) scale. Conduct experiments with low ratios to measure the effect of the VOC on ultimate ozone-forming potential.
- Conduct experiments with simple base ROG surrogates to provide the most sensitive and straightforward test of the mechanism. Conduct experiments with more complex surrogates to more closely respond to the ambient conditions.
- Vary the light source to test our understanding and ability to predictively model the photolytic processes that cause photochemical smog formation.

## Accomplishments

- Conducted reactivity experiments under high  $\text{NO}_x$ /base ROG conditions and used a simple ROG surrogate and a blacklight light source for a total of 39 VOCs. These included representative alkalines, aromatics, and oxygenates.
- Conducted reactivity experiments for nine VOCs with varying  $\text{NO}_x$  and ROG surrogate compositions.
- Constructed a new environmental chamber with a xenon arc light source to assess the effects of varying light source, which represents more closely the spectrum of sunlight than do the blacklights. Conducted preliminary runs with simple model systems and compared them with data using other chambers.
- Used the data to evaluate the chemical mechanism previously used to calculate the MIR reactivity scale and evaluate an updated version of the mechanism. The mechanisms simulated the results reasonably well, but there were some inconsistencies between model predictions and experimental data.



- Conducted incremental reactivity experiments using a xenon arc light source to assess light source effects on model predictions. Results indicate that the model correctly predicts light source effects on reactivity, after the mechanism was updated to appropriately represent effects of light source on aromatic reactivity.
- Conducted experiments to assess effects of humidity on environmental chamber results. No significant effects were observed.
- Conducted experiments to provide data needed to improve model predictions of reactivity differences among aromatic isomers, and to improve predictions of effects of light source on reactivities of aromatic hydrocarbons. These data were used to develop aromatic mechanisms to give better predictions of isomeric differences and light source effects.
- The data obtained are being used to develop and evaluate an updated, detailed mechanism for calculating VOC reactivity scales applicable to both mobile and stationary sources.

## Future Direction

The report on the final phase of this study is expected by March 1997.

## Publications

Carter, W.P.L., J.A. Pierce, I.L. Malkina, D. Luo, and W.D. Long. 1993. *Environmental Chamber Studies of Maximum Incremental Reactivities of Volatile Organic Compounds*, NREL Final Report.

Carter, W.P.L., D. Luo, I.L. Malkina, and J.A. Pierce. 1995. *Environmental Chamber Studies of Atmospheric Reactivities of Volatile Organic Compounds. Effects of Varying ROG Surrogate and NO<sub>x</sub>*, NREL Final Report.

Carter, W.P.L., D. Luo, I.L. Malkina, and J.A. Pierce. 1995. *Environmental Chamber Studies of Atmospheric Reactivities of Volatile Organic Compounds. Effects of Varying Chamber and Light Source*, NREL Final Report.

Carter, W.P.L., J.A. Pierce, D. Luo, and I.L. Malkina. 1995. "Environmental Chamber Studies of Maximum Incremental Reactivities of Volatile Organic Compounds", *Atmospheric Environment*, 29 (18), pp. 2499-2511.

Carter, W.P.L. 1995. "Computer Modeling of Environmental Chamber Measurements of Maximum Incremental Reactivities of Volatile Organic Compounds," *Atmospheric Environment*, 9 (18), pp. 2513-2527.

